# Selective Electrochemical Reductions of Aromatic Rings in the Presence of Olefinic Bonds[1]

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It was established that a nonconjugated, terminal, aliphatic olefin was not readily reduced when electrolyzed in a cell containing lithium chloride dissolved in methylamine as electrolyte. Under the same conditions, styrene was reduced quite cleanly to ethylbenzene. Nonconjugated, aromatic olefins (terminal or internal) with the double bond at least two carbon atoms removed from conjugation were reduced selectively to give 2,5-dihydro aromatic olefins as major products. Allylbenzene, depending upon the electrolysis conditions used, was reduced selectively to either *n*-propylbenzene or 2,5-dihydroallylbenzene. The latter olefin, in contrast to the behavior of other 2,5-dihydro aromatic types, was found to undergo a facile reduction to 2,5-dihydro-*n*-propylbenzene. When a terminal, aliphatic olefin was reduced in a divided electrochemical cell, appreciable alkane formation occurred accompanied by extensive isomerization of the double bond. A study of the base-catalyzed isomerization of 1-, *cis*-2-, and *cis*-4-octene was made.

The blue solution formed by dissolving an alkali metal in certain low molecular weight amines has been demonstrated to be an effective reducing agent for aliphatic olefins. With sodium in liquid ammonia containing an alcohol, terminal olefins[2,3] are reduced in moderate yield (*ca.* 40%) to alkanes, while internal, nonconjugated olefins undergo no reaction.[2,4] Similar results have been obtained in the lithium–ethylamine system,[5] although isomerization of the terminal bond often competed with the reduction process and the internal olefins thus formed were found to reduce only slowly. Lithium[6] in ethylenediamine at 90–100°, however, has been found to be an excellent reducing medium for the reduction of both terminal and internal olefins to alkanes in high yield (40–80%).

Previously,[7] it was shown that aromatic compounds could be reduced electrochemically in either a divided or an undivided electrolytic cell in a solution of lithium chloride dissolved in methylamine. Alkylbenzenes in the undivided cell (anode and cathode compartments not separated) were reduced to dihydro products in excellent yield. In the divided cell (anode and cathode separated by asbestos) the same alkylbenzenes were reduced equally well to tetrahydro products.

The above data suggested that terminal, nonconjugated double bonds might also be relatively resistant to electrochemical reduction, thereby permitting a selective reduction of aromatic rings in the presence of a side-chain olefinic bond. To this end, a series of alkyl and aryl olefins was reduced in the undivided cell. In addition, a representative terminal, aliphatic olefin was reduced in the divided cell in expectation that the more powerful reducing medium resulting from the change in cell design would duplicate the results obtained for the metal–amine reductions of terminal olefins.[5]

**1-Octene.**—Reduction of 1-octene in an undivided electrolytic cell[8] (consisting of an ordinary three-neck flask fitted with a Dry Ice condenser and two platinum electrodes with lithium chloride dissolved in methylamine as electrolyte) by passage of theoretical charge for reduction of one double bond gave only a small amount of saturated alkane (Table I, entry 1). When the reduction was carried out in the presence of ethanol, the yield of *n*-octane was increased somewhat (see Table I, entry 2), probably because ethanol is a better proton source for protonation of the anion intermediate than is monomethylamine.[9]

However, as can be seen (Table I, entry 3), the divided-cell reduction of 1-octene gave an appreciable amount of *n*-octane accompanied by extensive isomerization of the terminal olefin to its internal isomers. The latter, as have been shown previously,[1] are not readily reduced in this system.

The fact that reduction of a terminal olefin to alkane occurs to a much greater extent in the divided cell than in the undivided cell can be rationalized in terms of the relative amounts of solvated electrons in solution. The blue color (typical of alkali metals dissolved in low molecular weight amines), while present in the divided cell reduction, is absent when reduction is carried out in the undivided cell.

Thus, the electrochemical reduction of terminal, aliphatic olefins (if 1-octene can be taken as representative) to alkanes in the divided electrolytic cell[7,8] parallels the results obtained in alkali metal–amine systems previously reported.[2,3,5]

The isomerization that occurred in the divided-cell electrolysis can be attributed to a base-catalyzed isomerization of 1-octene by lithium methylamide. Since methylamine is the only source of protons during the reduction, the formation of one molecule of *n*-octane requires the formation of two molecules of lithium methylamide. It has been shown[7] that the function of the cell divider is to prevent the immediate destruction of lithium methylamide by the methylamine hydrochloride which forms at the anode. Therefore, the lithium methylamide remains in the cathode compartment and is available to catalyze the isomerization of 1-octene.

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[1] This in paper XI in a series entitled "Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines." See R. A. Benkeser and C. A. Tincher, *J. Org. Chem.*, **33**, 2727 (1968), for the previous paper in this series.

[2] H. Greenfield, R. A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, **76**, 1258 (1954).

[3] M. I. Rozhkova, I. V. Gostunskaya, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **118**, 299 (1958).

[4] T. J. King, *J. Chem. Soc.*, 898 (1951).

[5] A. P. Krapcho and M. E. Nadel, *J. Amer. Chem. Soc.*, **86**, 1096 (1964).

[6] L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

[7] R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, *J. Amer. Chem. Soc.*, **86**, 5272 (1964).

[8] Attention of the reader is directed to the fact, that, although the term "undivided" cell is employed throughout this work, in reality an ordinary, three-neck flask was employed. Hence, ordinary laboratory equipment is adequate to bring about the reactions described.

[9] A. P. Krapcho and A. A. Bothner-By, *ibid.*, **82**, 751 (1960), have suggested that the proton source is involved in the rate-determining step, at least in the reduction of aromatics by metal–ammonia systems.

TABLE I

ELECTROCHEMICAL REDUCTIONS OF 1-OCTENE

| | | | Product composition | | | | |
|---|---|---|---|---|---|---|---|
| Entry[a] | Cell | Ethanol | *n*-Octane, % | 1-Octene, % | *cis*-2-Octene, % | *trans*-2-Octene, % | *trans*-3-Octene, % |
| 1[b] | Undivided | None | 11 | 89 | 0 | 0 | 0 |
| 2[c,d] | Undivided | 0.2 mol | 20 | 80 | 0 | 0 | 0 |
| 3[e] | Divided | None | 51 | 2 | 30 | 10 | 7 |

[a] In all entries, 0.1 mol of 1-octene was electrolyzed with 19,300 C. [b] The product was analyzed on an Aerograph gas chromatograph using a 19-ft, 30% dibutyl tetrachlorophthalate column at 145°. [c] This run was identical in all respects with that described in entry 1 (see Experimental Section) except for the presence of the ethanol. A yield of 9.0 g (80%) of product was obtained, bp 118°. [d] The product was analyzed on an Aerograph gas chromatograph using a 20-ft, 25% Carbowax 1540 column at 90°. [e] The product was analyzed on an Aerograph gas chromatograph using a 25-ft, 25% $\beta,\beta'$-oxydipropionitrile column at 75° in conjunction with a 11-ft, 25% Carbowax 1540 column at 47°. Product identification was made by comparing retention times with authentic samples either obtained commercially (*n*-octane, 1-octene, *trans*-2-octene) or synthesized by known methods [K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 216, 2683 (1941)].

Some preliminary equilibrium and rate data[10] concerned with the isomerization of the *n*-octenes indicate that base catalysis[11] produces a stepwise migration of the double bond along the chain. To confirm that lithium methylamide in methylamine can cause the isomerization of 1-octene in our system (*i.e.*, methylamine solvent at −7°) and in the manner indicated by our results in the divided-cell reduction, a study of product composition *vs.* time was made for the amide-catalyzed isomerizations of 1-octene, *cis*-2-octene, and *cis*-4-octene. From the rate data shown[12] (Tables II–IV), it is clear that our results parallel those of previous work.[10] 1-Octene produces principally *cis*-2-octene initially.[13] When the double bond is buried in the chain (*e.g.*, *cis*-2-or *cis*-4-octene), the initial product consists principally of the olefin with the double bond one position removed from the starting material and *of the opposite configuration.* Thus *cis*-2-octene isomerized *initially* to *trans*-3-octene and *cis*-4-octene to *trans*-3-octene.

TABLE II

ISOMERIZATION OF 1-OCTENE

| Time, hr | 1-Octene, % | *trans*-2-Octene, % | *cis*-2-Octene, % | *trans*-3-Octene, % |
|---|---|---|---|---|
| 0 | 100.0 | 0.0 | 0.0 | 0.0 |
| 1[a] | 84.5 | Trace | 15.5 | |
| 2[a] | 65.8 | 5.4 | 28.8 | |
| 3[a] | 55.1 | 8.0 | 36.9 | |
| 6[a] | 33.2 | 11.5 | 55.3 | |
| 8[a] | 24.9 | 14.5 | 60.6 | |
| 29.5[a] | 11.4 | 21.0 | 67.6 | |
| 50[a] | 13.8 | 22.0 | 64.2 | |
| Work-up[b] | 0.0 | 23.6 | 58.2 | 18.2 |

[a] The sample was analyzed on an Aerograph gas chromatograph using a 20-ft, 25% Carbowax 1540 column at 60°. Under these conditions, *trans*-3-octene is not separable from 1-octene and hence is likely being formed earlier than is indicated in the table. [b] The sample was analyzed on an Aerograph gas chromatograph using three columns connected in series [8 m, 40% (by weight) of a saturated solution of $AgNO_3$ in $\beta,\beta'$-oxydipropionitrile on firebrick (60%) (I); 2 m, 40% (by wt) of a saturated solution of $AgNO_3$ in diethylene glycol on firebrick (60%) (II); and 8 m, 40% (by wt) of a saturated solution of $AgNO_3$ in diethylene glycol on firebrick (60%) (III)] at 37°.

TABLE III

ISOMERIZATION OF *cis*-2-OCTENE[a]

| Time,[b] hr | *cis*-2-Octene, % | *trans*-2-Octene, % | *trans*-3-Octene, % |
|---|---|---|---|
| 0 | 97.3 | 2.7 | 0.0 |
| 1 | 89.3 | 4.0 | 6.6 |
| 6 | 79.4 | 6.4 | 14.2 |
| 9 | 73.0 | 8.4 | 18.8 |
| 21 | 58.0 | 11.1 | 29.9 |
| 45 | 37.6 | 18.1 | 44.3 |
| Work-up | 25.1 | 22.6 | 52.3 |

[a] The procedure was identical with that described in the Experimental Section for 1-octene. The reagents consisted of *cis*-2-octene (2.08 g, 0.018 mol) and lithium methylamide (0.18 mol) prepared from 1.25 g of Li in 50 cc of methylamine. [b] The samples were analyzed at the intervals indicated on an Aerograph gas chromatograph using three columns connected in series at 37° (see Table II, footnote *b*).

TABLE IV

ISOMERIZATION OF *cis*-4-OCTENE[a]

| Time,[b] hr | *cis*-4-Octene, % | *trans*-3-Octene, % | *trans*-4-Octene, % |
|---|---|---|---|
| 0 | 98.0 | 0.0 | 2.0 |
| 4 | 83.6 | 12.6 | 3.7 |
| 20 | 54.7 | 36.8 | 6.7 |
| Work-up | 55.5 | 38.8 | 5.7 |

[a] The procedure was identical with that described in the Experimental Section for 1-octene. The reagents consisted of *cis*-4-octene (1.89 g, 0.017 mol) and lithium methylamide (0.16 mol) prepared from 1.14 g of Li wire in 50 cc of methylamine. [b] The samples were analyzed in the same manner as those in Table III.

**Aryl Olefins.**—The undivided-cell reductions of aromatic compounds to dihydro aromatics[7] and the fact that terminal and internal[1] olefins are relatively resistant to reduction under these conditions suggested that selective reductions of aromatic rings in the presence of double bonds might be achieved electrochemically.

Reduction of styrene in the undivided cell yielded ethylbenzene as major product. The product consisted of unreduced styrene (26%), ethylbenzene (69%), and 2,5-dihydroethylbenzene (5%). This result is not surprising, since conjugated double bonds are known to be readily reduced in metal–amine systems.[14]

As can be seen (Table V), the product composition resulting from the electroreduction of allylbenzene was dependent upon the presence or absence of ethanol. When the reduction was carried out in the normal manner by passage of the theoretical charge for reduction of one double bond (entry 1), *n*-propylbenzene was the major product. When the electrolysis was carried

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[10] M. D. Carr, J. R. P. Clarke, and M. C. Whiting, *Proc. Chem. Soc.*, 333 (1963).

[11] Lithium-2-aminoethylamide in ethylenediamine at 25° was employed.

[12] It must be emphasized at this point that equilibrium was not achieved (or intended) in the data of Tables II–IV.

[13] A. Schriesheim, J. E. Hofmann, and C. A. Rowe Jr., *J. Amer. Chem. Soc.*, **83**, 3731 (1961).

[14] R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

TABLE V

ELECTROCHEMICAL REDUCTIONS OF ALLYLBENZENE

| | | | Product composition[a] | | | |
|---|---|---|---|---|---|---|
| Entry[b] | Ethanol | Coulombs | Allylbenzene, % | *n*-Propylbenzene, % | 2,5-Dihydroallylbenzene,[c] % | 2,5-Dihydro-*n*-propylbenzene,[d] % |
| 1 | None | 19,180 | 21 | 55[e] | 7 | 15 |
| 2[f] | 0.2 Mol | 19,180 | 28 | 7 | 46 | 14 |
| 3[g] | 0.2 Mol | 36,000 | 2 | 1 | 38 | 52 |

[a] The products were analyzed on an Aerograph gas chromatograph using a 20-ft, 20% Zonyl E-7 column. [b] In all entries, 0.083 mol of allylbenzene, 0.8 mol of lithium chloride, and 500 cc of methylamine were used in the undivided electrolytic cell. [c] The nmr spectrum of 2,5-dihydroallylbenzene ($CCl_4$) showed a three-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a two-proton multiplet at 4.8–5.2, and a six-proton multiplet at 7.4. [d] The nmr spectrum of 2,5-dihydro-*n*-propylbenzene ($CCl_4$) showed a two-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a four-proton multiplet at 7.4, two-proton multiplets at 8.0 and 8.5, and a three-proton multiplet at 9.1. [e] Identity established by glpc retention time and ir spectra comparison with an authentic sample of *n*-propylbenzene. [f] This run was identical with that recorded in entry 1 (see Experimental Section) except for the presence of the ethanol. A yield of 9.3 g (95%) of product was obtained, bp 148–155°. [g] This run was identical with that recorded in entry 2 except for the number of coulombs employed. A yield of 8.5 g (85%) of product was obtained, bp 138–158°.

TABLE VI

ELECTROCHEMICAL REDUCTIONS OF 4-PHENYL-1-BUTENE

| | | | Product composition | | | |
|---|---|---|---|---|---|---|
| Entry[a] | Ethanol | Coulombs | 4-Phenyl-1-butene, % | *n*-Butylbenzene, % | 2,5-Dihydro-4-phenyl-1-butene,[b] % | 2,5-Dihydro-*n*-butylbenzene,[c] % |
| 1[d] | None | 19,300 | 50 | 6 | 29 | 8 |
| 2[d,e] | 0.2 mol | 19,180 | 35 | 0 | 47 | 11 |
| 3[f,g] | None | 21,000 | 8 | 14 | 48[h] | 30 |
| 4[d,i] | 0.11 mol | 19,300 | 7 | 0 | 52 | 34 |

[a] In entries 1 and 2, 0.1 mol of 4-phenyl-1-butene was used, and in entries 3 and 4, 0.05 mol of 4-phenyl-1-butene was used. [b] The nmr spectrum of 2,5-dihydro-4-phenyl-1-butene ($CCl_4$) showed a three-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a two-proton multiplet at 4.8–5.2, and two four-proton multiplets at 7.4 and 8.0. [c] The nmr spectrum of 2,5-dihydro-*n*-butylbenzene ($CCl_4$) showed a two-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a four-proton multiplet at 7.4, a two-proton multiplet at 8.0, a four-proton multiplet at 8.5, and a three-proton multiplet at 9.1. [d] The product was analyzed on an Aerograph chromatograph using a 20-ft, 25% Carbowax 1540 column. [e] This run was identical in all respects with entry 1 (see Experimental Section) except for the presence of the ethanol. A yield of 11 g (84%) of product was obtained, bp 120–172°. [f] The product was analyzed on an Aerograph chromatograph using a 20-ft, 20% Zonyl E-7 column. [g] In this run, the quantity of reactants was exactly one-half of those used in entry 1; namely, LiCl (17 g, 0.4 mol), 4-phenyl-1-butene (6.5 g, 0.05 mol), and anhydrous methylamine (300 cc). Also the reaction was carried out in a 0.5-l., three-neck flask instead of the usual 1-l. flask. The product obtained (bp 174°) amounted to 5 g (77%). [h] *Anal.* Calcd for $C_{10}H_{14}$: C, 89.48; H, 10.51. Found: C, 89.40; H, 10.65. [i] This run was identical with entry 3 except for the presence of the ethanol. A yield of 5.3 g (80%) of product was obtained.

out in the presence of ethanol (entry 2), however, 2,5-dihydroallylbenzene rather than *n*-propylbenzene was the predominant product.

The rather facile reduction of the terminal double bond to give *n*-propylbenzene is probably the result of a prior isomerization of the allylbenzene, caused by trace amounts of alkylamide that may be present, to form 1-phenylpropene, which is then reduced. In the presence of ethanol, which would react with any trace of alkylamide (thereby forming lithium ethoxide), isomerization of the double bond is impeded and the benzene ring undergoes preferential reduction. In substantiation of this assumption, it was established that lithium ethoxide does not catalyze the isomerization of allylbenzene under the reaction conditions which prevail during the electrochemical reduction of the latter compound.

2,5-Dihydro-4-phenyl-1-butene was the major product in all reductions of 4-phenyl-1-butene regardless of electrolysis conditions (Table VI). The major effect of ethanol was to eliminate the formation of *n*-butylbenzene entirely and to increase both current efficiency and the yields of reduction products.

Similarly, electrolysis of 5-phenyl-1-pentene in the presence of ethanol gave 2,5-dihydro-5-phenyl-1-pentene as the predominant product (63%).

The greatest selectivity for the reduction of an aromatic ring in the presence of a double bond was obtained in the reduction of 5-phenyl-2-pentene, wherein 83% of the product consisted of 2,5-dihydro-5-phenyl-2-pentene. No 2,5-dihydro-*n*-pentylbenzene was found.

The rather appreciable quantities of 2,5-dihydroalkylbenzene observed in the reductions of allylbenzene and 4-phenyl-1-butene when electrolyzed with approximately twice the theoretical amount of charge for reduction of one double bond (Table V, entry 3 and Table VI, entries 3 and 4) can be rationalized in terms of a reduction of the initially formed, nonconjugated, terminal, dihydroaromatic olefin. However, if the result obtained in the reduction of 1-octene (Table I) is representative for a nonconjugated, terminal olefin, the yields of such dihydroalkylbenzenes are much greater than would be predicted.

In an effort to resolve this difficulty, 2,5-dihydroallylbenzene, 2,5-dihydro-4-phenyl-1-butene, and 2,5-dihydro-5-phenyl-1-pentene were each reduced under essentially identical conditions. 2,5-Dihydroallylbenzene underwent a rather facile reduction, giving a 53% conversion into 2,5-dihydro-*n*-propylbenzene. 2,5-Dihydro-4-phenyl-1-butene and 2,5-dihydro-5-phenyl-1-pentene were converted into the corresponding 2,5-dihydroalkylbenzenes in 26 and 21% yield, respectively.

For 2,5-dihydroallylbenzene and, possibly, to a slight extent for 2,5-dihydro-4-phenyl-1-butene, these data point to the operation of some factor which causes an acceleration in the reduction rate of the terminal, nonconjugated double bond.[15]

One possible explanation for these results is that the radical-anion intermediate produced by the transfer of an electron to the terminal double bond of 2,5-dihydroallylbenzene is stabilized by interaction with one of the double bonds in the ring, thus lowering the activation energy for the reduction of this terminal double bond.[16]

**Mechanism.**—There are at least two obvious mechanistic pathways for the reductions we have carried out. One involves the transfer of an electron to the lithium cation to form a lithium atom followed by reduction of the olefin or aromatic ring by the solvated electrons arising from the metal. The alternative would be a direct electron transfer from the electrode to the olefin or aromatic ring to form the same radical-anion intermediate.

In most cases the former pathway appears to be the most probable both from stereochemical results[1] and polarographic studies[17] carried out on similar systems. In the case of a conjugated aryl olefin, like styrene, both processes may be possible, since recent polarographic studies[18,19] have shown that the reduction potential of the latter is close to that of the sodium cation.

## Experimental Section

**Reduction of 1-Octene. A. Undivided Cell.**—The undivided electrolytic cell previously described[7,8] was charged with lithium chloride (34 g, 0.8 mol), 1-octene (11.2 g, 0.1 mol), and 600 cc of anhydrous methylamine. A current of 2 A was passed through the cell for 2 hr and 41 min (19,300 C). Solvent was then allowed to evaporate through a water condenser and the resulting residue was hydrolyzed with water (350 cc). The aqueous solution was extracted with pentane and the latter extracts were dried ($CaSO_4$), concentrated, and distilled to give 5.9 g (52%) of product, bp 100–114°. The product composition is shown in Table I (entry 1).

**B. Divided Cell.**—1-Octene (11.2 g, 0.1 mol) was placed in the cathode compartment of a divided electrolytic cell.[7] Current (2 A) was passed through the cell for 2 hr and 41 min (19,300 C). After electrolysis, the asbestos divider was broken, and the solvent was evaporated through a water condenser. The remainder of the procedure was identical with that described above. A yield of 4.6 g (42%) was obtained. The composition of this product is listed in Table I (entry 3).

**Isomerization of 1-Octene (Table II).**—Lithium methylamide (0.48 mol) was prepared by adding 0.33 g of lithium wire to a solution of methylamine (500 cc) containing a catalytic amount of ferric chloride. Then 1-octene (11.2 g, 0.1 mol) was added, the mixture stirred, and aliquots removed at intervals. These were hydrolyzed with water and extracted with pentane. The pentane extracts were analyzed by glpc. After 50 hr, the solvent was allowed to evaporate, and the residue was worked up in the usual manner. The results are shown in Table II.

**Reduction of Styrene (Undivided Cell).**—Styrene (10.4 g, 0.1 mol) was reduced in the undivided electrolytic cell[7] by passing a current of 2 A through the system for 2 hr and 41 min (19,300 C). Distillation, following the usual work-up, yielded 7.6 g (73%) of product, bp 120–128°. Analysis by glpc (6-ft, 25% $\beta,\beta'$-oxydipropionitrile column, 70°) showed the product to be 69% ethylbenzene, 5% 2,5-dihydroethylbenzene, and 26% styrene. Identification was made by comparing retention times of each of the compounds with those of authentic samples. In addition, the ir spectrum of the ethylbenzene component was identical with that of an authentic sample.

**Reduction of Allylbenzene (Table V). Undivided Cell.**—Allylbenzene[20] (9.8 g, 0.083 mol) was reduced in the undivided electrolytic cell[7] by passing a current of 2 A through the cell for 2 hr and 40 min (19,180 C).

Solvent was then evaporated through a condenser that was kept at 0°. The residue was hydrolyzed, and the organic material was isolated in the usual manner. Distillation afforded 8.2 g (84%) of product boiling at 140–155°. The product composition is shown in Table V (entry 1).

**Attempted Isomerization of Allylbenzene with Lithium Ethoxide.**—Lithium wire (0.6 g, 0.087 g-atom) and absolute ethanol (13.8 g, 0.3 mol) were placed in a three-neck, 1-l. flask fitted with a mechanical stirrer and a Dry Ice condenser. The mixture was stirred until all of the lithium had dissolved and a white slurry of lithium ethoxide had formed. At this point, allylbenzene (12 g, 0.1 mol) and methylamine (600 cc) were added, and the mixture was stirred for 3 hr. Water (5 cc) was then added to destroy the ethoxide. After solvent evaporation, the residue was hydrolyzed (water). The usual work-up produced 9.0 g (75%) of product. Analysis by glpc (20-ft, 25% Carbowax 1540 column, 140°) showed that no isomerization to propenylbenzene had occurred.

**Reduction of 4-Phenyl-1-butene (Table VI). Undivided Cell.**—4-Phenyl-1-butene[21] (13.2 g, 0.1 mol) was electrolyzed in the undivided cell[7] with a current of 2 A for 2 hr and 41 min (19,300 C). After solvent removal through a water condenser and the usual work-up, distillation yielded 11 g (84%) of product (bp 150–174°). See Table VI (entry 1).

**Reduction of 5-Phenyl-1-pentene. Undivided Cell, Ethanol Present, Excess Charge.**—Electrolysis of 5-phenyl-1-pentene[22] (7.3 g, 0.05 mol) in the presence of absolute ethanol (5 g, 0.1 mol) was carried out in the undivided cell[7] by passing a current of 2 A for 2 hr and 40 min (19,180 C). There was obtained 6.5 g (89%) of product, which by analysis by glpc (20-ft, 25% Carbowax 1540 column, 160°) was shown to contain 5-phenyl-1-pentene (15%), 2,5-dihydro-5-phenyl-1-pentene[23] (63%), and 2,5-dihydro-*n*-pentylbenzene[24] (14%).

**Reduction of 5-Phenyl-2-pentene. Undivided Cell, Ethanol Present, Excess Charge.**—5-Phenyl-2-pentene[25] (3.5 g, 90% *cis*, 10% *trans*), absolute ethanol (3 g, 0.07 mol), 300 cc of anhydrous methylamine, and lithium chloride (8.5 g, 0.2 mol) were placed in a 500-cc flask and electrolyzed by the passage of current (2 A) for 1 hr and 20 min (9500 C). Analysis of the product (2.5 g, 83%), boiling at 205–210°, by glpc (20 ft, 25% Carbowax 1540 column) indicated the presence of 5-phenyl-*cis*-2-pentene (7%), 2,5-dihydro-5-phenyl-*cis*-2-pentene (75%), and 2,5-dihydro-5-phenyl-*trans*-2-pentene[26] (8%).

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[15] The possibility that the terminal double bond was initially isomerized into conjugation with a double bond of the ring followed by a 1,4 reduction seems unlikely for at least two reasons. First, the presence of a large excess of ethanol during these reductions would minimize the formation of alkylamide, which could catalyze such an isomerization. Second, it would seem that if such an isomerization did occur, isomerization of the double bonds in the ring should also have occurred, forming some 2,3-dihydro-*n*-propylbenzene or possibly even a monoolefin upon further reduction. None of these materials was detected.

[16] See B. R. Ortiz de Montellano, B. A. Loving, T. C. Shields, and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3365 (1967), for results which may be related to this postulate.

[17] H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Electrochem. Soc.*, **113**, 1060 (1966).

[18] J. D. Anderson, *J. Polym. Sci., Part A-1*, **6**, 3185 (1968).

[19] N. Yamazaki, S. Nakahama, and S. Kambara, *ibid., Part B*, **3**, 57 (1965).

[20] E. B. Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

[21] H. Gilman and J. H. McGlumphy, *Bull. Soc. Chim. Fr.*, **43**, 1326 (1928); C. N. Riiber, *Ber.*, **44**, 2392 (1911).

[22] J. V. Braun, H. Deutsch, and A. Schmatloch, *Ber.*, **45**, 1255 (1912); T. W. Campbell and A. C. Haven Jr., *J. Appl. Polym. Sci.*, **1**, 73 (1959).

[23] The nmr spectrum of this compound ($CCl_4$) showed a three-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a two-proton multiplet at 4.8–5.2, two four-proton multiplets at 7.4 and 8.0, and a two-proton multiplet at 8.4.

[24] The nmr spectrum of this compound ($CCl_4$) showed a two-proton multiplet at $\tau$ 4.3, a one-proton multiplet at 4.6, a four-proton multiplet at 7.4, a two-proton multiplet at 8.0, a six-proton multiplet at 8.5, and a three-proton multiplet at 9.1.

[25] E. M. LaCombe and B. Stewart, *J. Amer. Chem. Soc.*, **83**, 3457 (1961), prepared this compound by a pyrolytic method. Our synthesis involved coupling benzylmagnesium chloride with crotyl chloride. From the isomeric mixture of products which resulted, we separated 3.5 g of a mixture consisting of 90% *cis*- and 10% *trans*-5-phenyl-2-pentene, utilizing preparative gas chromatography (15-ft, 24% Carbowax 20 M column). The identity of these isomers was established by matching their ir and nmr spectra with those of authentic samples.[1]

[26] The nmr spectrum ($CCl_4$) of 2,5-dihydro-5-phenyl-2-pentene (*cis* or *trans*) showed a two-proton multiplet at $\tau$ 4.3, a three-proton multiplet at 4.6, two four-proton multiplets at 7.4 and 8.0, and a three-proton multiplet at 8.4.

*Anal.* Calcd for $C_{11}H_{16}$ (2,5-dihydro-5-phenyl-*cis*-2-pentene): C, 89.19; H, 10.81. Found: C, 89.39; H, 10.79.

**Reduction of 2,5-Dihydroallylbenzene. Undivided Cell, Ethanol Present.**—Lithium chloride (5 g, 0.12 mol), absolute ethanol (4 g, 0.09 mol), and 2 g of material (87% 2,5-dihydroallylbenzene and 13% 2,5-dihydro-*n*-propylbenzene)[27] were placed in a 100-cc three-neck flask along with 60 cc of methylamine. A current of 0.5 A was passed through the system for 1 hr and 46 min (3180 C). The product, 1.8 g (90%), was shown by glpc (4-ft, LAC 446 column, 60°) to consist of 2,5-dihydroallylbenzene (34%) and 2,5-dihydro-*n*-propylbenzene (66%) as adjudged by their respective retention times.

*Anal.* Calcd for $C_9H_{12}$ (2,5-dihydroallylbenzene): C, 89.94; H, 10.06. Found: C, 89.96; H, 10.09.

**Reduction of 2,5-Dihydro-4-phenyl-1-butene. Undivided Cell, Ethanol Present.**—Lithium chloride (5 g, 0.12 mol), absolute ethanol (4 g, 0.09 mol), and 1.5 g of material (90% 2,5-dihydro-4-phenyl-1-butene, 5% 2,5-dihydro-*n*-butylbenzene, and 5% 4-phenyl-1-butene)[28] were electrolyzed in a 100-cc three-neck flask by passing a current (0.5 A) for 76 min (2280 C). There was obtained 1.2 g (80%) of material consisting of 2,5-dihydro-*n*-butylbenzene (31%) and 2,5-dihydro-4-phenyl-1-butene (69%). These compounds were identified by matching their retention times (glpc) with the products obtained from the reductions of 4-phenyl-1-butene (Table VI).

**Reduction of 2,5-Dihydro-5-phenyl-1-pentene. Undivided Cell, Ethanol Present.**—In a manner completely analogous to that described above for the dihydro-1-butene, 1.3 g of material[29] [2,5-dihydro-5-phenyl-1-pentene (95%) and 5-phenyl-1-pentene (5%)] was electrolyzed by passing a current (0.5 A) for 59 min (1770 C). The product (1.2 g, 91%) consisted of (analysis by glpc, 20-ft, 25% Carbowax 1540 column, 150°) 5-phenyl-1-pentene (3%), 2,5-dihydro-5-phenyl-1-pentene, (76%), and 2,5-dihydro-*n*-pentylbenzene (21%).

*Anal.* Calcd for $C_{11}H_{16}$ (2,5-dihydro-5-phenyl-1-pentene): C, 89.19; H, 10.81. Found: C, 89.15; H, 10.95.

**Registry No.**—(2,5-Dihydro-5-phenyl)-*cis*-2-pentene, 21893-20-9; 2,5-dihydroallylbenzene, 21902-31-8; (2,5-dihydro-5-phenyl)-1-pentene, 21902-32-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *cis*-4-octene, 7642-15-1; allylbenzene, 300-57-2; 4-phenyl-1-butene, 768-56-9.

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[27] This material was obtained by preparative glpc (a combination of a 15-ft, 24% Zonyl E-7 column and a 15-ft 24% Carbowax 20 M column was used) from the products of the reactions described in Table V.

[28] A mixture obtained by preparative glpc (same columns and conditions as described in ref 27) from the products of the reactions summarized in Table VI.

[29] Obtained by preparative glpc (same columns and conditions as described in ref 27) from the products of reduction of 5-phenyl-1-pentene.

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# Reaction of Alkyl Iodides with Peracetic Acid in the Presence of Aromatic Compounds[1]

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Treatment of *n*-alkyl iodides with peracetic acid in the presence of aromatic compounds in acetic acid at 30° affords alkyl acetates and often iodo aromatic compounds in good yields. The rate of the reaction for a mixture of methyl iodide, peracetic acid, and *m*-xylene can be expressed as $v = k[CH_3I][CH_3CO_3H]$ and is independent of the concentration of *m*-xylene. The structure of alkyl iodides affects the yield of iodoaromatic compound in the decreasing order *n*-alkyl > *sec*-alkyl > *t*-alkyl. The reaction mechanism is briefly discussed in terms of the effect of structure on the kinetics and product composition.

Among the reactions of alkyl iodides, the substitution of iodide by nucleophilic reagents such as hydroxide, phenoxide, alkoxide, and halide ions and other solvent molecules has been studied extensively.[2] The kinetic studies on oxidation with peracids which have electrophilic oxygen have been reported, *e.g.*, epoxidation of olefins and oxidation of aldehydes, ketones, amines, aromatic hydrocarbons, and sulfur compounds.[3,4] Also, oxidation of iodide ion by peracids or by peroxides has been used as a standard method for the quantitative analysis of peroxides or peracids.[5,6] During our kinetic study of iodoacetoxylation of olefins, it was observed that alkyl iodides liberate iodine on treatment with peracetic acid.[7] However, few reports have thus far appeared on the oxidation of alkyl iodides with peracids.[8]

There are several methods for iodination of aromatic compounds with molecular iodine, and these reactions usually require oxidizing agents such as nitric acid, periodic acid, sulfur trioxide, peroxides, or silver sulfate.[9,10] We have previously suggested an aromatic iodination with a mixture of iodine and peracetic acid and postulated a mechanism explaining its autocatalytic nature.[9]

We have found that molecular iodine in the above reaction can be replaced by alkyl iodide in some cases, and we wish to report in the present paper a novel aromatic iodination with a mixture of alkyl iodides and peracetic acid in acetic acid, which is exemplified by

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[1] Contribution No. 132.

[2] (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapters 6 and 7, pp 157–185; (b) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, Chapter 8, pp 250–305; (c) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 7, pp 306–418; (d) D. Segaller, *J. Chem. Soc.*, **103**, 1154 (1913); (e) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 2, pp 61–163; (f) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963; (g) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956).

[3] D. Swern, *ibid.*, **45**, 1 (1949).

[4] J. B. Lee and B. C. Uff, *Quart. Rev.* (London), 429 (1967).

[5] A. G. Davies, "Organic Peroxides," Butterworth and Co. Ltd., London, 1961, p 138.

[6] J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin Inc., New York, N. Y., 1964, Chapter 5.

[7] Y. Ogata and K. Aoki, *J. Org. Chem.*, **31**, 1625 (1966).

[8] (a) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 789; (b) J. B. Dence and J. D. Roberts, *J. Org. Chem.*, **33**, 1251 (1968); (c) D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

[9] Y. Ogata and K. Aoki, *J. Amer. Chem. Soc.*, **90**, 6187 (1968).

[10] (a) J. K. Kochi, B. M. Graybill, and M. Kurz, *ibid.*, **86**, 5257 (1964); (b) L. S. Silvert, D. Swern, and T. Asahara, *J. Org. Chem.*, **33**, 3670 (1968); (c) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworth and Co. Ltd., London, 1959.